X-ray photoelectron and absorption spectroscopy investigation of Se^{IV} and Sb^{V} reduction by mackinawite

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Both Se and Sb exist in nature in a wide range of oxidation states and can be potential hazardous contaminants depending on their speciation and reactivity. While Se typically occurs as oxyanions (SeO_3^{-2} and SeO_4^{-2}) in oxic conditions, it can be reduced by Fe^{II} containing minerals such as mackinawite (FeS) to Se^0 and Se^{-II} [1, 2]. Similarly, Sb occurs in several oxidations states (-III, 0, III, V) and is shown to strongly adsorb to Fe oxide minerals as $Sb(OH)_6^-$ and subsequently reduced to the more mobile form $Sb(OH)_3(aq)$ [3]. In this study we employed cryogenic-XPS and XAS techniques in order to understand the redox processes involving Se^{IV} and Sb^{V} at the surface of mackinawite.

Fe 2p XPS spectrum of pure mackinawite surface revealed presence of both Fe^{II}-S and Fe^{III}-S species and the proportion of the latter increased when reacted to Se^{IV} suggesting oxidation of surface Fe^{II}. In addition, presence of elemental S at the surface of the reacted sample suggested oxidation of sulfur as well. Corresponding Se K-edge XANES spectra of the reacted sample confirmed reduction of Se with the formation of FeSe. These results suggest that Se reduction is coupled to both S^{-II}/S^0 and Fe^{II}/Fe^{III} redox half reactions.

Sb 3d spectrum of the reacted sample revealed that Sb^{V} was completely reduced to Sb^{III} at the surface of mackinawite. However, the S 2p spectrum of the reacted sample remained largely unchanged except for a slight increase in surface monosulfide content. This suggests that in contrast to the Se^{IV}-mackinawite system, S did not take part in the redox reaction involving Sb^{V}. The Fe 2p spectrum, however, showed a distinct shoulder of Fe^{III}-species indicating oxidation of surface Fe^{II}. Corresponding Sb K-edge EXAFS of the reacted sample confirmed that the Sb^{III} was coordinated to three sulfur atoms at a distance of 2.5 Å as in Sb_2S_3, which most likely explains the slight increase in the surface monosulfide content in the S 2p spectrum.

These results demonstrate the importance of surface mediated redox reactions in controlling the fate of toxic contaminats such as Se and Sb in soil and groundwater.

[1] Charlet *et al.* (2007) *GCA* **71**, 5731-5749. [2] Scheinost & Charlet (2008) *ES&T*, online. [3] Scheinost *et al.* (2006) *GCA* **70**, 3299-3312.

Biogeochemical tracers of modern and ancient life in seafloor lavas

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Stikingly similar micron-sized, microbially generated, tubular alteration structures have been discovered in the glassy rims of pillow basalts and inter-pillow hyaloclastites from both modern and exceptionally well preserved Archean seafloor lavas. These structures are interpreted to have initially formed by microbial etching of originally glassy material. In ancient samples, microbial alteration structures are subsequently mineralized by titanite and suggest the basaltic Archean seafloor was colonized by microbes early in Earth's history. Comparison of the Archean tubular structures to microbial alteration textures in modern MORB glass shows striking similarities. Petrographic observations, overlapping metamorphic and magmatic ages from the pillow lavas, as well as direct dating of the titanite by *in situ* laser ablation multi-collector-ICP-MS demonstrates the titanite ($CaTiSiO_4$) in ancient samples is of Archean age and implies the microbial alteration process occurred soon after eruption. Disseminated carbonates within microbially altered pillow rims have C-isotope values depleted by as much as –20‰, which is consistent with microbial oxidation of organic matter. X-ray mapping indicates concentrations of biologically important elements such as C, N, P, K, and S occur along the margins of the tubular structures in both modern and ancient samples. We have recently characterized modern samples at the nanometer scale with Scanning Transmission X-ray Microscopy to map carbon speciation and iron redox state within the microbial alteration channels in modern samples. New N-isotope data on the same modern samples suggests microbial N-isotope biosignatures may also be preserved. Although textural evidence is preserved in undeformed, low grade, meta-volcanic rocks, biogeochemical tracers are more robust and may survive stronger deformation and metamorphic conditions over geological timescales.